There is a paucity of data concerning the conformational idiosyncrasies of spiro structures. Theoretical calculations indicate that bond angle distortions of the type present in spiro compounds are important in conformational equilibria.[35] The limited number of reports concerning spiro structures indicate marked deviations from trends in open-chain analogs.[36] The significant reduction in the amount of twist conformer in 3,3:6,6-bis(tetramethylene)-*s*-tetrathiane (VII) as compared to duplodithioacetone (VI) is evidence of the uniqueness of the spiro analog. The preference for the chair form in VII is consistent with a preliminary X-ray crystallographic study indicating the presence of the chair form.[37]

The results of a study of the solvent dependence of the twist/chair ratio in duplodithioacetone (Table II) are not unexpected, *i.e.*, no appreciable solvent effect. It is noteworthy that in a nonpolar solvent (*trans*-1,2-dichloroethylene) and a highly polar solvent (*cis*-1,2-dichloroethylene), the chair:twist ratio is the same.

Experimental Section

Nmr spectra were recorded using a Varian A-60 spectrometer equipped with a V-6040 temperature controller. Temperature was measured using a methanol or ethylene glycol sample.

Duplodithioacetone was prepared according to the method of Magnusson.[17] *Anal.* Calcd for $C_6H_{12}S_4$: C, 33.95; H, 5.70; S, 60.02. Found: C, 33.98; H, 5.83; S, 60.02.

3,3:6,6-Bis(tetramethylene)-*s*-tetrathiane was prepared according to the method of Magnusson.[17] *Anal.* Calcd for $C_{10}H_{16}S_4$: C, 45.41; H, 6.10; S, 48.49. Found: C, 45.44; H, 6.14; S, 48.59.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

Acknowledgment. We thank the Research Corporation (Frederick Gardner Cottrell Grant) and the National Science Foundation (COSIP Grant) for partial support of this work.

---

[35] J. B. Hendrickson, *J. Am. Chem. Soc.*, **84,** 3355 (1962).

[36] (a) R. A. Carlson and N. S. Behn, *Chem. Commun.*, 339 (1968); (b) J. J. Uebel, *Tetrahedron Letters*, 4751 (1967).

[37] D. S. Breslow and H. Skolnik, "Multi-Sulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles," Part Two, Interscience Publishers, New York, N. Y., 1966, p 629.

Cage Effects and Activation Volumes for Homolytic Scission Reactions[1,2]

Robert C. Neuman, Jr., and Joseph V. Behar

Contribution from the Department of Chemistry, University of California at Riverside, Riverside, California 92502. *Received May 14, 1969*

Abstract: The effects of pressure on the rates of solution phase decomposition of the *t*-butyl peresters of phenylacetic acid, cyclohexanecarboxylic acid, and benzoic acid have been determined, as well as the pressure dependence of the product distributions of the first two peresters. In cumene at 79.6°, the observed activation volumes are *t*-butyl perbenzoate, +10 cc/mole; carbo-*t*-butylperoxycyclohexane, +3.9 cc/mole; and *t*-butyl phenylperacetate, +1 to +3 cc/mole. The data are used to demonstrate that observed activation volumes are abnormally high for homolytic scission reactions in which cage recombination of the primary radical products can occur to regenerate starting material. Product data support the mechanistic proposals and additionally permit calculations of crude values for the difference in activation volumes for radical combination, disproportionation, and diffusion.

Solution phase decomposition of radical initiators such as azo compounds, diacyl peroxides, and peresters often gives less than a stoichiometric yield of kinetically free radicals which can initiate polymerization, autoxidation, or other radical reactions. This apparent inefficiency in radical production indicates that the radical pair arising from a molecule of initiator remains in a solvent shell long enough to undergo bimolecular coupling or disproportionation reactions in competition with separative diffusion.[3]

This manifestation of the cage effect has long been recognized and studied because of its kinetic visibility. Another potential manifestation of the cage effect, not readily observable, is illustrated in eq 1 using *t*-butyl peroxide (DBO) as the example. While the ultimate yield of kinetically free *t*-butoxy radicals from DBO is

$$t\text{-buO–O-}t\text{-bu} \underset{k_c}{\overset{k_1}{\rightleftarrows}} \overline{t\text{-buO}\cdot\ \cdot\text{O-}t\text{-bu}} \xrightarrow{k_d} 2t\text{-buO}\cdot \quad (1)$$

quantitative, the apparent rate constant for DBO decomposition is not necessarily equal to that for homolytic scission (k_1). Rather it is given by the expression in eq 2 and will approach k_1 only when $k_c <<< k_d$.

$$k_{\text{obsd}} = k_1\left[\frac{k_d}{k_c + k_d}\right] \quad (2)$$

This specific operation of the cage effect to bring about a regeneration of the free-radical initiator after homolytic scission has been the subject of debate for many years; however, it has only been recently experimentally verified. Martin showed by ^{18}O-labeling studies that such recombination was significant in the

---

[1] (a) High Pressure Studies. IV. Part III: R. C. Neuman, Jr., and R. J. Bussey, *Tetrahedron Lett.*, 5859 (1968). (b) Support by the National Science Foundation (GP-4287, GP-7349, and GP-8670) is gratefully acknowledged.

[2] Portions of this study have appeared as preliminary communications: (a) R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **89,** 4549 (1967); (b) R. C. Neuman, Jr., and J. V. Behar, *Tetrahedron Lett.*, 3281 (1968); (c) R. C. Neuman, Jr., and J. V. Behar, Abstracts of the 154th Meeting of the American Chemical Society, Chicago, Ill., Sept 10–15, 1967, S-163.

[3] See H. P. Waits and G. S. Hammond, *J. Amer. Chem. Soc.*, **86,** 1911 (1964).

thermal decomposition of acetyl peroxide,[4] and Pryor,[5] Traylor,[6] and Walling[7] have demonstrated the existence of this "internal return"[5] in the decomposition reactions of some azo compounds and dialkyl peroxides (including DBO) by examining the effect of solvent viscosity on decomposition rates.

Several years ago we embarked on a study of the effect of pressure on homolytic scission reactions. Although the original intention of this work was not directed toward an investigation of the cage effect it quickly became clear that our observations were relevant to the question of free-radical "internal return" and also would require a reinterpretation of conclusions derived from other high-pressure studies of homolytic scission reactions.

Apparent activation volumes reported for homolytic scission reactions[8–11] prior to our studies are given in Table I. For a single-step reaction, the activation volume[12] is related to the pressure dependence of the rate constant (eq 3) and positive activation volumes signify

$$\partial \ln k/\partial P = -\Delta V^*/RT \qquad (3)$$

a decrease in reaction rate with an increase in pressure.[13] These data (Table I) have led to the generalization that values of ΔV^* for homolytic scission are in the region of +10 cc/mole.[13]

Table I. Apparent Activation Volumes for Homolytic Scission Reactions

Compound	Solvent	T, °C	ΔV_{obsd}, cc/mole	Ref
Benzoyl peroxide	CCl_4	60	+10	8
	CCl_4	70	9	8
	Acetophenone	80	5	9
t-Butyl peroxide	Benzene	120	13	10
	CCl_4	120	13	10
	Cyclohexene	120	7	10
	Toluene	120	5	10
Pentaphenylethane	Toluene	70	13	11
AIBN[a]	Toluene	70	4	11

[a] Azobisisobutyronitrile.

These activation volumes, however, were determined from the pressure dependence of the apparent rate constant for decomposition of the initiator. In the general scheme for such a reaction k_{obsd} is not necessarily equal to k_1, the rate constant for homolytic scission (eq 2). Hence, using eq 2 as a model, it is immediately apparent that the activation volume for homolytic scission (ΔV_1^*) is not necessarily equal to the apparent activation volume for initiator decomposition ($\Delta V_{\mathrm{obsd}}^*$) (eq 4 and 5).

$$\partial \ln k_{\mathrm{obsd}}/\partial P = \partial \ln k_1/\partial P - \partial \ln (1 + k_c/k_d)/\partial P \qquad (4)$$

$$\Delta V_{\mathrm{obsd}}^* = \Delta V_1^* + RT\partial \ln (1 + k_c/k_d)/\partial P \qquad (5)$$

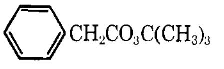
This will only be true when "internal return" does not occur (k_c equals zero).[14] For the initiators in Table I, with the exception of AIBN, available data now indicate that k_c can be greater than zero.[15,16]

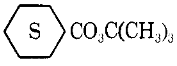
Thermal decomposition of *t*-butyl peresters has been extensively studied by Bartlett[17] and his data indicate that primary homolytic scission can occur by either a one-bond or multiple-bond pathway (eq 6 and 7) depending on the group R.[18]

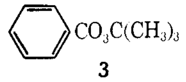
$$RCO_2O\text{-}t\text{-bu} \longrightarrow \overline{RCO_2\cdot \; \cdot O\text{-}t\text{-bu}} \qquad (6)$$

$$RCO_2O\text{-}t\text{-bu} \longrightarrow \overline{R\cdot CO_2\cdot O\text{-}t\text{-bu}} \qquad (7)$$

One would expect that recombination of the primary radical pair produced in the one-bond scission systems (eq 6) could occur to regenerate perester ($k_c > 0$); however, this would be unlikely for the multiple-bond scission peresters (eq 7) leading effectively to a zero value for k_c. In the latter cases, the apparent activation volumes would thus be equal to the true values for homolytic scission (ΔV_1^*). The following results from a high-pressure study of the thermal decomposition reactions of *t*-butyl phenylperacetate (**1**), carbo-*t*-butylperoxycyclohexane (**2**), and *t*-butyl perbenzoate (**3**) support this hypothesis.


1


2


3

Experimental Section

Solvents. Reagent grade cumene (Matheson Coleman and Bell) was purified by repeated treatment with concentrated sulfuric acid, washed successively with water, 10% aqueous sodium carbonate, and water, dried over anhydrous magnesium sulfate, and distilled under a nitrogen atmosphere. It was stored in a brown bottle under an atmosphere of nitrogen. Reagent grade chlorobenzene

---

[4] J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 3650 (1966).

[5] (a) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967); (b) W. A. Pryor and K. Smith, Abstracts of the 155th Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, P-76.

[6] H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967).

[7] C. Walling and H. Waits, *J. Phys. Chem.*, **71**, 2361 (1967).

[8] A. E. Nicholson and R. G. W. Norrish, *Discussions Faraday Soc.*, 22, 138 (1956).

[9] C. Walling and J. Pellon, *J. Amer. Chem. Soc.*, **79**, 4786 (1957).

[10] C. Walling and G. Metzger, *ibid.*, **81**, 5365 (1959).

[11] A. H. Ewald, *Discussions Faraday Soc.*, 22, 138 (1956).

[12] The activation volume (ΔV^*) for a single-step reaction represents the effective volume difference between the transition state and reactants. It reflects changes both in internal geometry and solvent interactions.[13]

[13] For reviews of the theory see: (a) S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press, New York, N. Y., 1957; (b) M. G. Gonikberg, "Chemical Equilibrium and Reaction Rates Under Pressure," Moscow, 1960; English translation available from Office of Technical Services, U. S. Department of Commerce (NASA TT F-95), and from Oldbourne Press, London; (c) R. S. Bradley, Ed., "High Pressure Physics and Chemistry," Vol. I and II, Academic Press, New York, N. Y., 1963; (d) S. D. Hamann, *Ann. Rev. Phys. Chem.*, 15, 349 (1964); (e) E. Whalley, *Advan. Phys. Org. Chem.*, 2, 93 (1964); (f) W. J. Le Noble, *Progr. Phys. Org. Chem.*, 5, 207 (1967); (g) E. Whalley, *Ann. Rev. Phys. Chem.*, **18**, 205 (1967); (h) K. E. Weale, "Chemical Reactions at High Pressure," E. and F. N. Spon Ltd., London, 1967; U. S. distribution by Barnes and Noble, Inc., New York, N. Y.

[14] The quantity $\Delta V_{\mathrm{obsd}}^*$ will be equal to ΔV_1^* even when k_c is not equal to zero if $\ln (1 + k_c/k_d)$ is pressure independent. Subsequent discussion will indicate, however, that this would be a most unlikely occurrence.

[15] (a) Direct evidence is available for *t*-butyl peroxide.[6,7] Studies of acetyl peroxide[4] provide strong support for nonzero values of k_c for benzoyl peroxide. Studies of AIBN indicate that it decomposes by a concerted two-bond scission pathway.[3] Evidence that recombination of a *t*-butoxy, benzoyloxy radical pair can occur (the internal return process from **3**) is provided by studies of Koenig and Deinzer on N-nitroso-N-benzoyl-O-*t*-butylhydroxylamine.[15b] (b) T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, **88**, 4518 (1966).

[16] Walling discussed the solvent dependence of $\Delta V_{\mathrm{obsd}}^*$ for *t*-butyl peroxide in terms of the possibility of nonzero values of k_c for geminate *t*-butoxy radicals.[10] However, the implication of his analysis to other homolytic scission reactions has been generally ignored. This has been probably due in part to the lack of independent evidence, now available, supporting recombination of geminate *t*-butoxy radicals.[6,7]

[17] For leading references see J. P. Lorand and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 3294 (1966).

[18] (a) P. D. Bartlett and R. R. Hiatt, *ibid.*, 80, 1398 (1958); (b) P. D. Bartlett and D. M. Simons, *ibid.*, 82, 1753 (1960); (c) P. D. Bartlett and C. Rüchardt, *ibid.*, 82, 1756 (1960).

(Matheson Coleman and Bell) and pentane were purified in the same manner with the substitution of anhydrous calcium chloride for magnesium sulfate. Pentane was stored over molecular sieves. Reagent grade tetrahydrofuran was refluxed over lithium aluminum hydride and distilled and stored under nitrogen.

Reagents. Reagent grade pyridine (Matheson Coleman and Bell) was refluxed over barium oxide for 3 days, distilled at atmospheric pressure, and stored in a brown bottle over reagent grade potassium hydroxide pellets. A 90% aqueous solution of *t*-butyl hydroperoxide (Lucidol Corp.) was distilled under reduced pressure to remove the water, bp 34–35° (18–20 mm) (lit.[18a] bp 20–20.5° (5 mm)). Iodimetric titration indicated a purity of 95%. It was stored at −15°. *t*-Butyl perbenzoate (Matheson Coleman and Bell) was used without further purification.

Phenylacetic Acid. Hydrolysis of phenylacetonitrile in aqueous acid gave a 97% yield of phenylacetic acid.[19] Recrystallization from 95% ethanol yielded material with a melting point of 75–76° (lit.[19] mp 76–76.5°); infrared 5.9 μ (C=O) (lit.[18a] 5.9 μ).

Phenylacetyl Chloride. This acid chloride was prepared in 86% yield by the method of Truitt, *et al.*[20]: bp 94–97° (12 mm) (lit.[10] bp 94–96° (12 mm)); infrared 5.6 μ (C=O) (lit.[21] 5.6 μ).

***t*-Butyl Phenylperacetate.** This perester was synthesized by the method of Bartlett and Hiatt[18] with the following modifications. To a 250-ml erlenmeyer flask were added 100 ml of pentane, 9.3 g (0.0602 mole) of phenylacetyl chloride, and 6.3 g (0.07 mole) of *t*-butyl hydroperoxide. The mixture was cooled to −20° using a Dry Ice–isopropyl alcohol mixture. Subsequently, 4.76 g (0.0602 mole) of pyridine was added dropwise and the mixture was allowed to stand until the precipitation of pyridinium chloride was complete. The reaction mixture was stirred for an additional 0.5 hr at *ca.* −25°. It was then poured over 100 g of ice and the pentane layer was washed sequentially with 10% H_2SO_4, 10% Na_2CO_3, and water. It was dried over anhydrous magnesium sulfate and stored in the freezer at *ca.* 0° for 1 hr. The $MgSO_4$ was removed by filtration and the pentane was evaporated on a rotary evaporator below 0°, giving 9 g of a colorless oil, yield 71.8% based on acid chloride. A 1-g sample of the oil was chromatographed on a 2 × 20 cm column of 200 mesh Florisil using pentane as the eluent. Eight fractions, 20 ml each, were collected. The pentane was removed on a rotary evaporator under reduced pressure. Most of the product was recovered in the second, third, and fourth fractions. The chromatography procedure was repeated two more times and 0.92 g was recovered; infrared 5.61 μ (C=O) (lit.[18a] 5.58–5.61 μ). The material was stored in the freezer (*ca.* −15°) and it crystallized after several hours. Its rate of thermal decomposition in chlorobenzene at 79.6° was essentially identical with that reported by Bartlett under the same conditions (see Results).

***t*-Butyl Benzyl Ether.** Treatment of benzyl chloride (Matheson Coleman and Bell) with sodium *t*-butoxide in tetrahydrofuran gave a 25% yield of the ether:[22] bp 85–87° (12 mm) (lit.[22] bp 98° (20 mm)); nmr singlets at 71, 259, and 430 Hz (reference TMS), with relative areas of 9:2:5, respectively.

Bibenzyl. A zone-refined sample was provided by Dr. Kenji Kawoka.

Bicumyl. Thermal decomposition of *t*-butyl peroxide (Matheson Coleman and Bell) in cumene gave bicumyl;[23] it was recrystallized from 95% ethanol, mp 116.5–117.5° (lit.[23] mp 117–118°).

Cyclohexylcarbonyl Chloride. A 12.7-g (0.1 mole) sample of cyclohexanecarboxylic acid (Matheson Coleman and Bell) and 23.8 g (0.2 mole) of thionyl chloride (Matheson Coleman and Bell) were placed in a 100-ml round-bottomed flask fitted with a drying tube and reflux condenser and heated on a steam bath overnight. Excess thionyl chloride was removed using a rotary evaporator and the residue distilled under reduced pressure: bp 85–89° (30 mm) (lit.[24] bp 83–89°) (30–35 mm)); yield 85.3%.

Carbo-*t*-butylperoxycyclohexane. This perester[24] was prepared from cyclohexanecarbonyl chloride by the same procedure used for *t*-butyl phenylperacetate with the exception that the reaction mixture was held at 0–5° and the reaction time was 4 hr; yield 78%; infrared 5.6 μ (C=O).

***t*-Butyl Cyclohexyl Ether.** Reaction of the Grignard reagent of bromocyclohexane with *t*-butyl perbenzoate gave a 69% yield of ether:[25] bp 59–61° (15 mm) (lit.[25] bp 55–57° (10 mm)); nmr singlet at 72 Hz, broad multiplet at 78–120 Hz, broad singlet at 216 Hz (reference TMS); relative areas of peaks at 72 and 78–120 to that at 216 were 19:1.

High-Pressure Apparatus. The basic apparatus consisting of a pressure-generating and -measuring panel and a high-pressure vessel was purchased from the Harwood Engineering Co., Walpole, Mass. The apparatus is rated up to 200,000 psi and the internal cavity of the vessel measures approximately 1 in. in diameter by 9 in. in depth. The high-pressure hydraulic fluid used was Bayol 35, a gift of the Humble Oil Co. The basic apparatus is essentially identical with that described by Professor W. Le Noble.[26]

The high-pressure vessel is suspended in a constant-temperature bath permitting temperature control to ±0.04°. The bath was maintained at 79.58 ± 0.04° during these studies. The upper temperature limit of this system is approximately 100°, and this is dictated by the volatility of the high-pressure fluid.

Sample Cells. The samples of reaction mixture decomposed at high pressures were contained in small sample cells constructed from Teflon spaghetti tubing (0.130 in. i.d., 0.155 in. o.d.; R. S. Hughes and Co., Los Angeles). The tubing was cut in lengths of 1.5 in. and the ends were sealed with Teflon plugs. The plugged ends were covered with the small portion of no. 07 rubber serum stopples and each cell was sealed in several evacuated polyethylene bags to avoid contamination of the reaction mixture by high-pressure fluid. Such contamination was an infrequent occurrence and was detectable in the infrared spectrum of the sample. Contaminated samples were discarded. The sample cells had a volume of *ca.* 0.25 cc and could be used for several kinetic runs before irreversible deformation occurred.[27]

Kinetic Runs. A master solution of perester in cumene or chlorobenzene was prepared (*ca.* 0.1 *M*) and stored in a freezer under a nitrogen atmosphere. Samples were taken from the master solution for each kinetic run. Infrared analyses showed that no decomposition of the master solution occurred during the period in which it was being used to obtain kinetic data.

In a typical kinetic run, two Teflon cells were filled with master solution, immersed in the vessel, and pressurized. The initial pressure obtained was always higher than the equilibrium pressure due to adiabatic heating of the high-pressure fluid during pressurization.[28] Pressure equilibration was always reached within 15 min after immersion of the sample. After pressure equilibration, the samples were kept in the apparatus for varying periods of time. Each high-pressure run generated one kinetic point.

Great care was taken to duplicate the procedure beginning with immersion through pressurization for each kinetic run at a particular pressure. This was essential since the zero-time sample, used for analysis of each kinetic point, was taken at a fixed arbitrary time after pressure equilibration. In order to achieve reproducibility, each step of the procedure was timed. Control experiments in which the zero-time sample was collected in several kinetic runs indicated that the technique was satisfactory since the experimental variation in zero-time readings led to less than 1% spread in the value of the rate constant. Pressure release, and removal and quenching of the sample, were accomplished within 2–3 min in each run and led to no significant error in the rate constants.[28]

Some kinetic runs at atmospheric pressure were carried out on samples in the Teflon cells, while others were performed using sealed glass ampoules. No significant variation in the resulting rate constants was observed when the two methods were compared.

It was impractical to degas samples contained in the Teflon cells. However, a comparison of the atmospheric pressure rate constant for **1** in chlorobenzene with that obtained by Bartlett (see Results) suggests that the presence of oxygen did not complicate these data. In particular, when cumene was used as the solvent it is most probable that oxygen was rapidly scavenged from the solution in the sample cell by the well-known chain reaction yielding cumene hydroperoxide. The latter was detected as a reaction product in these systems.

Kinetic Analysis. The rates of decomposition of the various peresters were followed by monitoring the intensity of the perester carbonyl band in the infrared spectral region (5.6 μ).[18] Spectra

---

(19) R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 436.

(20) P. Truitt, D. Mark, L. M. Lang, and J. Jeanes, *J. Amer. Chem. Soc.*, 70, 4214 (1948).

(21) Sadtler Standard Spectra, Vol. 5, No. 4575, Sadtler Research Labs.

(22) H. Normont and T. Cuvigny, *Bull. Soc. Chim. Fr.*, 1866 (1965).

(23) C. Walling and R. Rabinovitz, *J. Amer. Chem. Soc.*, **81**, 1137 (1959).

(24) P. D. Bartlett and R. E. Pincock, *ibid.*, **84**, 2445 (1962).

(25) S. O. Lawesson and N. C. Yang, *ibid.*, **81**, 4230 (1959).

(26) W. J. Le Noble, *ibid.*, **85**, 1470 (1963).

(27) Personal communication from Professor C. Walling and Dr. T. Augurt. See C. Walling and T. A. Augurt, *ibid.*, **88**, 4163 (1966).

(28) See ref 13f, pp 217–218.

were recorded on a Perkin-Elmer 621 grating infrared spectrometer using 0.1-mm sodium chloride cells.

All kinetic samples were stored in the freezer between the time of the kinetic run and infrared analysis and all of the points used to determine a single rate constant were analyzed at one time. The spectrometer was carefully adjusted prior to the analyses and an infrared spectrum of a sample of master solution was recorded. No significant variation in the perester carbonyl transmittance value could be detected for the master solution throughout the runs in which it was used. True transmittance values were determined for each kinetic sample, and these values were used to obtain rate constants by means of the relationship shown in eq 8.[18] The quantities T_∞, T_0, and T are the transmittance readings for the perester carbonyl band (5.6 μ) in the infinite time sample (>10 half-lives), the zero-time sample, and the intermediate samples (corresponding to the time t), respectively. Values of k were determined by least-squares analysis.

$$kt = 2.3 \log \frac{[\log (T_\infty/T_0)]}{[\log (T_\infty/T)]} \qquad (8)$$

The slow rate of thermal decomposition of *t*-butyl perbenzoate (**3**) precluded the determination of values of T_∞. Relative rate constants for the decomposition of **3** at 1 and 4000 atm were calculated from one-point kinetic data by two alternative methods. Method A is based on the pseudo-zero-order approximation for low conversions (eq 9–12). The values of t for the kinetic points at 1 and 4000 atm were identical (*ca.* 70 hr) and with the assumption that T_∞ was independent of pressure the expression in eq 13 arises from eq 12 and allows direct calculation of the rate constant ratio k_1/k_{4000}. Method B does not require the assumption of low conversion (eq 9) but involves the assumption that all values of T_∞ are equal to one. Thus eq 8 becomes eq 14 and the ratio k_1/k_{4000} can be directly obtained from the individual values of k_pt which are calculated from eq 14.

$$-\mathrm{d}(P)/\mathrm{d}t \simeq k(P)_0 \qquad (9)$$

$$kt \simeq [(P)_0 - (P)]/(P)_0 \qquad (10)$$

$$(P)_0/(P) = [\log (T_\infty/T_0)]/[\log (T_\infty/T)] \qquad (11)$$

$$kt = [\log (T/T_0)]/[\log (T_\infty/T_0)] \qquad (12)$$

$$k_1/k_{4000} = \log (T/T_0)_1/\log (T/T_0)_{4000} \qquad (13)$$

$$kt = 2.3 \log \left[\frac{\log (1/T_0)}{\log (1/T)}\right] \qquad (14)$$

Product Analysis. The products were determined by glpc analyses of the infinite-time kinetic samples. The yields of *t*-butyl alcohol and acetone from decomposition of *t*-butyl phenylperacetate in chlorobenzene, and the yields of cyclohexane and cyclohexene from decomposition of carbo-*t*-butylperoxycyclohexane in cumene, were determined using an F & M Model 700 gas chromatography instrument with W filaments containing a 9 ft × 0.25 in. column packed with 15% Carbowax 400 on Chromosorb W (oven temperature 65°); helium was the carrier gas. The yields of all other products (including *t*-butyl alcohol from *t*-butyl phenylperacetate in cumene and from carbo-*t*-butylperoxycyclohexane in cumene) were determined using an F & M Model 700 gas chromatography instrument with WX filaments equipped with an F & M Model 240 power proportioning temperature programmer. This instrument contained a matched pair of 6 ft × 1/8 in. columns packed with 10% SE-30 on 80-100 AW DMCS-700; helium was the carrier gas. For all analyses the columns were held at 65° for 4 min after sample injection and then temperature programmed to 220° at a rate of 10°/min.

Products were identified by comparison with authentic samples and quantitatively determined by comparison with standard solutions containing authentic samples of the products.

Results

***t*-Butyl Phenylperacetate.** Rate constants for the thermal decomposition (79.6°) of *t*-butyl phenylperacetate (**1**) were determined at several pressures in the solvents cumene and chlorobenzene by monitoring the perester carbonyl band in the infrared (Table II). Some representative kinetic plots are shown in Figure 1. Bartlett has reported a rate constant of 1.05×10^{-4} sec^{-1} for decomposition of **1** at 79.55° in chlorobenzene at atmospheric pressure.

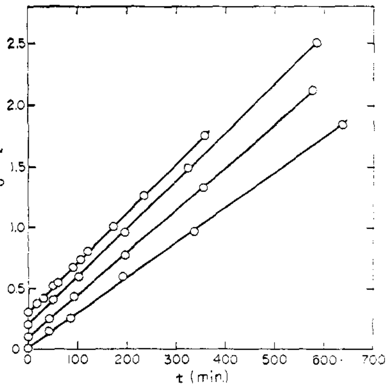


Figure 1. First-order kinetic plots for the thermal decomposition (79.6°) of *t*-butyl phenylperacetate in cumene as a function of pressure. The line terminating at the origin is for 6000 atm and each successive line (4000, 2000, and 1 atm) has been displaced upward from the origin.

The pressure dependence of the decomposition rate constant in the solvent cumene is shown in Figure 2. The curvature indicates that ΔV^* is pressure dependent and this precludes easy extraction of a single value which can be assigned as the activation volume. Thus, two-point activation volumes are reported in Table II comparing each high-pressure rate constant with the value at atmospheric pressure ($\Delta V_{0,p}^*$) and comparing adjacent pressure points ($\Delta V_{P_1,P_2}^*$).

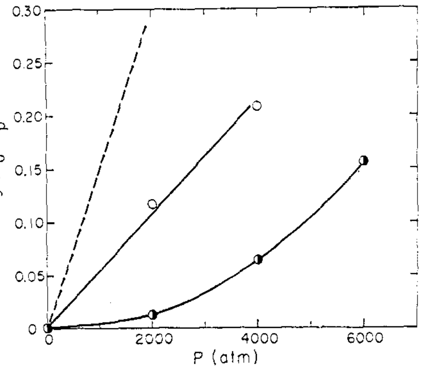


Figure 2. The pressure dependence of the first-order rate constants for thermal decomposition (79.6°) in cumene of *t*-butyl phenylperacetate (◑) and carbo-*t*-butylperoxycyclohexane (○). The dashed line represents an activation volume of +10 cc/mole.

The products of the decomposition of **1** in cumene and chlorobenzene were determined by glpc analysis. In addition to those for which quantitative data are available (Table III), both bicumyl and α,α-dimethylbibenzyl (benzylcumyl) were formed in cumene; stilbene and benzaldehyde were formed in low yields in chlorobenzene.

Carbo-*t*-butylperoxycyclohexane. Kinetic data for the thermal decomposition of **2** in cumene (79.6°) as a function of pressure are given in Table IV. These data yield an activation volume of +3.9 ± 0.5 cc/mole (Figure 2).

Table II. Rate Constants and Activation Volumes for the Decomposition of *t*-Butyl Phenylperacetate in Cumene and Chlorobenzene (79.6°)

P, atm	Solvent	$k \times 10^4$, sec^{-1}	$\Delta V_{o,p}^*$,[a] cc/mole	$\Delta V_{P_1,P_2}^*$,[b] cc/mole
1	Cumene	0.678 ± 0.002		
2000		0.657 ± 0.003	0.5	0.5
4000		0.584 ± 0.007	1.1	1.7
6000		0.473 ± 0.007	1.7	3.1
1	Chlorobenzene	1.02 ± 0.05		
2000		0.95	1.0	
4000		0.90 ± 0.01	1.0	

[a] Calculated from the equation $\Delta V_{o,p}^* = (RT/P) \ln (k_o/k_p)$ where the quantity k_o is the rate constant at atmospheric pressure. [b] Calculated from the equation $\Delta V_{P_1,P_2}^* = [RT/(P_2 - P_1)] \ln (k_{P_1}/k_{P_2})$.

Table III. Product Yields from the Decomposition of *t*-Butyl Phenylperacetate in Cumene and Chlorobenzene (79.6°)

	% yield[a]			
	Cumene		Chlorobenzene	
Product	1 atm	4000 atm	1 atm	4000 atm
t-Butyl alcohol	70	50	30	44
Acetone	Trace	Trace	50	28
Benzyl *t*-butyl ether	21.4	50.0	13	34
Total *t*-butoxy	91.4	100.0	93	106
Benzyl *t*-butyl ether	21.4	50.0	13	34
Bibenzyl	27.0	12.0	33	30
Toluene	6.4	12.0	Trace	Trace
Total benzyl[b]	>54.8	>74.0	>46	>64

[a] Determined by glpc. [b] In cumene, α,α-dimethyldibenzyl and bicumyl were formed in significant yields, but not quantitatively determined. In chlorobenzene, stilbene and benzaldehyde were detected but not quantitatively determined.

Table IV. Kinetic Data for Decomposition of Carbo-*t*-butylperoxycyclohexane in Cumene (79.6°)

Pressure, atm	$k \times 10^5$, sec^{-1}
1	1.86 ± 0.06
2000	1.42
4000	1.15 ± 0.03

Table V. Product Yields from Decomposition of Carbo-*t*-butylperoxycyclohexane in Cumene (79.6°)

	% yield[a,b]		
Product	1 atm	2000 atm	4000 atm
t-Butyl alcohol	72.3	60.8	52.6
t-Butyl cyclohexyl ether	17.2	(25)	33.1
Total *t*-butoxy	89.5	(86)	85.7
t-Butyl cyclohexyl ether	17.2		33.1
Cyclohexane	57.0		29.2
Cyclohexene	12.8		28.4
Total cyclohexyl	87.0		90.7

[a] Determined by glpc. [b] α-Cumylcyclohexane detected but not quantitatively determined.

The products arising from the decomposition reaction of **2** were determined by glpc and their yields as a function of pressure are given in Table V.[29]

***t*-Butyl Perbenzoate.** Relative rate constants for the thermal decomposition of *t*-butyl perbenzoate (**3**) were determined at pressures of 1 and 4000 atm at a temperature of 79.6° in cumene and chlorobenzene. At this temperature the decomposition rate of **3** is very slow[18a] and the relative rate constants were determined from only single kinetic points assuming a first-order rate law. The relative rate constants were calculated by two alternative methods involving different assumptions (see Experimental Section). The first method (labeled method A) was based on the pseudo-zero-order approximation for low conversions and does not require infinite time samples since T_∞ disappears from the equations. The second method (method B) utilized the integrated first-order rate equation (eq 8) with the assumption that T_∞ would be equal to one in all cases. The relative rate constants and two-point activation volumes ($\Delta V_{1,4000}^*$) obtained from analysis by methods A and B are given in Table VI.

No correction was applied for adiabatic heating during pressurization of the 4000-atm samples of **3** (see Experimental Section). Such a correction would lead to larger values of k_1/k_{4000}. Additionally, the occurrence of induced decomposition cannot be excluded.[30] Since this process would be pressure accelerated,[31] its presence would lead to abnormally low values of k_1/k_{4000}. It is reasonable, then, to assume that correction of the data for these complications could only *raise* the values of ΔV^* reported in Table VI.

Table VI. Kinetic Data for the Decomposition of *t*-Butyl Perbenzoate in Cumene and Chlorobenzene (79.6°)

	Method A[a]		Method B[a]	
Solvent	k_1/k_{4000}	ΔV_{obsd}^*, cc/mole	k_1/k_{4000}	ΔV_{obsd}^*, cc/mole
Cumene	4.23	+10.4	3.99	+10.0
Chlorobenzene	5.97	+12.9	5.62	+12.5

[a] See text and Experimental Section.

Discussion

Extensive studies of perester decomposition reactions at atmospheric pressure have led to their grouping into one-bond and concerted multiple-bond scission pathways.[18] The available data indicate that *t*-butyl perbenzoate (**3**) decomposes by the former pathway (eq 6)[18a] and that *t*-butyl phenylperacetate (**1**)[18] and carbo-*t*-butylperoxycyclohexane (**2**)[18a,24] decompose by a concerted two-bond scission mechanism (eq 7). Based on the analysis previously outlined (eq 2 and 5), it would be predicted that the observed activation volumes (ΔV_{obsd}^*) for the latter systems would be equal to the true activation volumes for homolytic scission (ΔV_1^*), while ΔV_{obsd}^* for **3** would differ from ΔV_1^* by the quantity $RT\partial \ln (1 + k_c/k_d)/\partial P$ (eq 5).

The probable *qualitative* pressure dependence of the expression $\ln (1 + k_c/k_d)$ can be predicted from the observed variation in the product distributions for **1** and **2** with pressure. The basic reaction sequence describing product formation from the geminate pair produced from **1** is shown in Scheme I. Since reaction of diffused *t*-butoxy radicals with the solvent cumene to produce *t*-butyl alcohol must be quantitative (*vide infra*), the pressure dependence of the ratio k_c'/k_d' can be determined from the pressure dependence of the ether/*t*-butyl alcohol ratio. The data in Table III for **1** in cumene show that this ratio increases from *ca.* 0.3 at 1 atm to 1.0

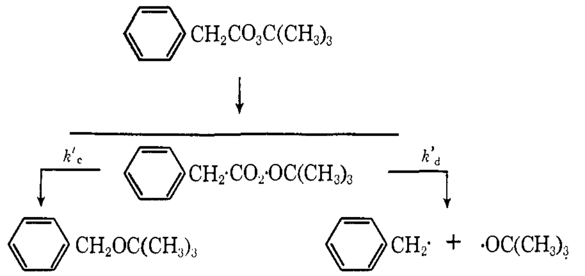
---

(29) An additional product was detected, but not quantitatively determined, which we believe to be α-cumylcyclohexane.

(30) A. T. Blomquist and A. F. Ferris, *J. Amer. Chem. Soc.*, **73**, 3408 (1951).

(31) See ref 13h, pp 217–218.

Scheme I

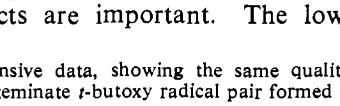


at 4000 atm. The same general trends are observed for the products of **1** in chlorobenzene and **2** in cumene (*vide infra*).[32]

These observations support the general contention[13] that bimolecular radical coupling reactions (k_c) are pressure accelerated and that diffusion processes (k_d) are pressure retarded leading to an increase in k_c/k_d, and hence in ln $(1 + k_c/k_d)$, with an increase in pressure. Since the quantity $RT\partial \ln (1 + k_c/k_d)/\partial P$ will thus be greater than zero, it is predicted that in systems with nonzero values of k_c, ΔV_{obsd}^* will be greater than ΔV_1^*.

A comparison of the values of ΔV_{obsd}^* for **1** (+1 to +3 cc/mole) and **2** (+4 cc/mole) with those for **3** (+10 to +13 cc/mole) supports this analysis. Since benzoyl peroxide, *t*-butyl peroxide, and pentaphenylethane decompositions should also be characterized by nonzero values of k_c,[15] it is probable that the large values of ΔV_{obsd}^* previously reported for them (Table I) are significantly greater than the activation volumes for their homolytic scission (ΔV_1^*).[33] It is well known, however, that thermal decomposition of azobisisobutyronitrile (AIBN) occurs by simultaneous two-bond scission[15] and hence the reported activation volume of +4 cc/mole (Table I) most certainly represents ΔV_1^*. The similarity of this value for AIBN to the values of ΔV_{obsd}^* for **1** and **2** lends further support to these hypotheses.

These data, and other preliminary results obtained in our laboratory, suggest that values of ΔV_1^* for two-bond scission initiators are on the order of +4 cc/mole. While the data for *t*-butyl phenylperacetate (**1**) decomposition give even lower values for ΔV_1^* we suggest that these results, and the unusual pressure dependence of the decomposition rate constant (see Figure 2) for **1**, are the result of polar effects. It has been proposed that the transition state for decomposition of **1** has polar character (**4**)[18c] and it might be expected that such a contribution would be less important in the decomposition of **2** from a simple consideration of the relative stabilities of benzyl and cyclohexyl carbonium ions. The greater decomposition rate of **1** in the more polar solvent chlorobenzene compared to cumene (Table II) suggests that solvation effects are important. The low activation volume *and* the unusual pressure dependence (Figure 2) may thus be a reflection of solvent electrostriction in the transition state (an accelerating effect) superimposed on the rate-retarding volume expansion due to homolytic scission.[34] This proposal is supported by the preliminary data from pressure studies of various ring-substituted derivatives of **1**.[35]



4

The observed activation volumes for homolytic scission reactions in which the primary radical products may undergo internal return are determined by both the pressure dependence of k_1 and k_c/k_d. The relationship between the various rate constants at 1 atm and some pressure P is given by eq 15 which can be derived from

$$\frac{k_{obsd}^{\,o}}{k_{obsd}^{\,P}} = \left(\frac{k_1^{\,o}}{k_1^{\,P}}\right)\left(\frac{1 + (k_c/k_d)_P}{1 + (k_c/k_d)_o}\right) \qquad (15)$$

the dependence of k_{obsd} on k_1 and k_c/k_d (eq 2). While extensive data are not available, it is informative to calculate values of $(k_c/k_d)_{4000\ atm}$ which satisfy the experimental value of $(k_{obsd}^{\,o}/k_{obsd}^{\,4000})$ for *t*-butyl perbenzoate (**3**) (Table VI) *assuming* that $(k_1^{\,o}/k_1^{\,4000})$ has a value such that ΔV_1^* is equal to +4 cc/mole.[36] The results of this analysis for a range of reasonable values of $(k_c/k_d)_o$ are given in Table VII. The resulting values of $(k_c/k_d)_{4000}$ have been used in conjunction with eq 16 to calculate

$$\ln [(k_c/k_d)_P/(k_c/k_d)_o] = (\Delta V_d^* - \Delta V_c^*)_P P/RT \quad (16)$$

two-point values for $\Delta V_d^* - \Delta V_c^*$, and these are also included in Table VII.[36b] The important conclusion to be drawn is that these latter values, while varying with the choice of $(k_c/k_d)_o$, are consistent with experience (*vide infra*).[1a]

Table VII. Values of the Ratio k_c/k_d for *t*-Butyl Perbenzoate Decomposition[a]

$(k_c/k_d)_o$	$(k_c/k_d)_{4000}$	$(\Delta V_d^* - \Delta V_c^*)_{4000}$[b]
0.1	1.5	+20
0.3	2.0	14
0.5	2.5	12
1.0	3.6	9

[a] Calculated using eq 15 and the values given in ref 36. [b] Units of cubic centimeters per mole.

The product data for **1** and **2** as a function of pressure (Tables III and V) are readily interpreted in terms of the expected free-radical reactions and their pressure dependences.[37] These data indicate that induced decomposition, and other alternative decomposition modes such as the Criegee rearrangement, processes expected to be pressure accelerated, are unimportant.

---

[32] More extensive data, showing the same qualitative trend, is available for the geminate *t*-butoxy radical pair formed from di-*t*-butyl hyponitrite.[1a]

[33] (a) The origin of the low values of ΔV_{obsd}^* for *t*-butyl peroxide in cyclohexene and toluene (Table I) is not clear.[7] These data may reflect a solvent dependence of the quantity $RT\partial \ln (1 + k_c/k_d)/\partial P$, and further investigations are in progress. The low activation volume for benzoyl peroxide in acetophenone may be the result of experimental difficulties.[9,33b] (b) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, Jr., *J. Amer. Chem. Soc.*, 87, 518 (1965).

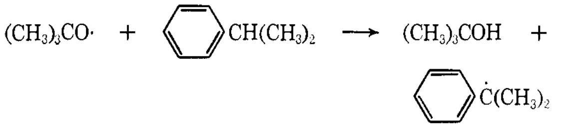
[34] This is a well-known phenomenon in pressure studies of SN1 solvolysis reactions.[13]

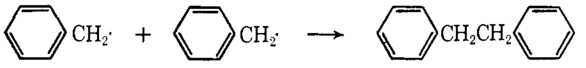
[35] R. C. Neuman, Jr., and J. V. Behar, unpublished results.

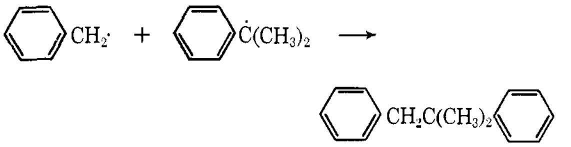
[36] (a) The value of $(k_{obsd}^{\,0}/k_{obsd}^{\,4000})$ used in the calculations was 4.0, corresponding to a ΔV_{obsd}^* of +10 cc/mole (see Table VI). The value of $(k_1^{\,0}/k_1^{\,4000})$ corresponding to a ΔV_1^* of +4 cc/mole is 1.75 and this was used in the calculations. While the choice of this value was based on data for initiators in which two bonds are breaking in the transition state, the simultaneous shortening of the C–O or N–N bond in the incipient CO_2 or N_2 produced from peresters or azo compounds, respectively, suggests that it might be a reasonable approximation to ΔV_1^* for one-bond initiators. (b) This analysis ignores cage decarboxylation of benzoyloxy radicals. The rate constant k_d can be thought of as a sum of those for decarboxylation and diffusion. Each of these processes competes with internal return and each is pressure retarded.

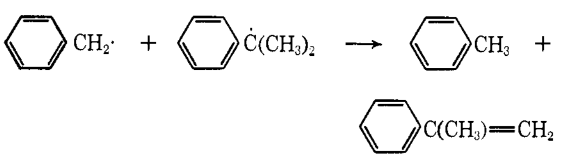
[37] The advent of glpc has permitted the determination of more extensive product data than those available from the early studies of **1** and **2**.[18a–c,24]

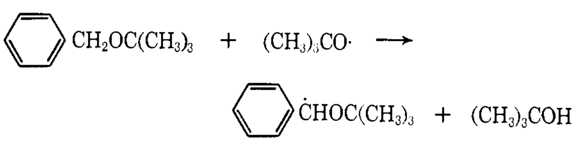
Some of the chemistry occurring subsequent to the decomposition of **1** has been outlined in Scheme I. In cumene, the virtual absence of acetone indicates that diffused *t*-butoxy radicals rapidly react with the solvent to produce *t*-butyl alcohol and cumyl radicals (eq 17). Diffused benzyl radicals apparently undergo bimolecular coupling reactions with themselves or with cumyl radicals to produce, respectively, bibenzyl and benzylcumyl (eq 18 and 19). Toluene most reasonably arises from a disproportionation reaction of a benzyl and cumyl radical leading simultaneously to α-methylstyrene (eq 20), and the coupling of two cumyl radicals gives bicumyl. The effect of pressure on the ratio of *t*-butyl benzyl ether to *t*-butyl alcohol has been previously discussed and agrees with the anticipated pressure dependence of the rate constant ratio k_c'/k_d' (Scheme I). The data, while limited, permit calculation of a two-point value for $\Delta V_d^* - \Delta V_c^*$ of +10 cc/mole. The product data for **1** in chlorobenzene are complicated by the absence of readily abstractable solvent hydrogen atoms. This leads to significant β scission of *t*-butoxy radicals yielding acetone,[38] and a reduction in the yield of *t*-butyl benzyl ether due to hydrogen abstraction by *t*-butoxy radicals (eq 21). The radical resulting from this reaction (eq 21) should undergo β scission and the observation of benzaldehyde formation (Table III) supports this hypothesis.[39]


(17)


(18)

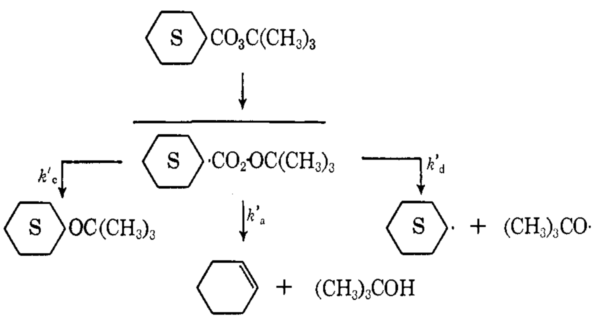

(19)


(20)


(21)

Thermal decomposition of carbo-*t*-butylperoxycyclohexane (**2**) in cumene gives cage products and solvent-separated radicals by the pathways outlined in Scheme II. In contrast to reactions available to the geminate radical pair from **1** (Scheme I), that from **2** may undergo both a coupling reaction (k_c') and a disproportionation reaction (k_a'). As in the case of **1** in cumene, it is anticipated that the sole fate of diffused *t*-butoxy radicals is *t*-butyl alcohol formation (eq 17). Similarly, cumyl radicals may dimerize giving bicumyl.

Scheme II



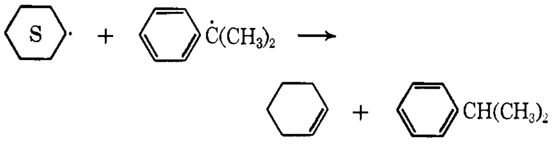
If cyclohexene is formed only by the disproportionation reaction (k_a') shown in Scheme II, the product data may be used to calculate the quantities $\Delta V_d^* - \Delta V_c^*$ and $\Delta V_d^* - \Delta V_a^*$ from the rate constant ratios defined in eq 22 and 23, respectively. The data in Table V

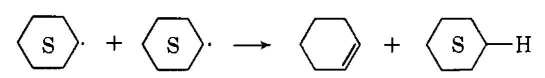
$$k_c'/k_d' = (\text{ether})/[(t\text{-butyl alcohol}) - (\text{cyclohexene})] \quad (22)$$

$$k_a'/k_d' = (\text{cyclohexene})/[(t\text{-butyl alcohol}) - (\text{cyclohexene})] \quad (23)$$

yield values of +11 and +12 cc/mole, respectively. The value for $\Delta V_d^* - \Delta V_c^*$ is very similar to the analogous quantity obtained from the pressure dependence of the products from **1**, and it is also apparent the activation volumes for radical coupling and disproportionation are very similar ($\Delta V_c^* - \Delta V_a^*$ *ca.* +1 cc/mole).

However, cyclohexene can also be formed in at least two other reactions potentially available to *diffused* cyclohexyl radicals (eq 24 and 25). While these reactions cannot be definitely excluded at this time[40] we suggest that the following arguments support the contention that virtually all of the cyclohexene arises as shown in Scheme II. (1) The exothermic hydrogen abstraction from cumene by cyclohexyl radicals, or cyclohexylation of cumene, are both favored by the massive concentration of cumene; (2) the alternate disproportionation reaction of the cyclohexyl and cumyl radicals to yield cyclohexane and α-methylstyrene would be energetically more favorable; and (3) the pressure dependence of the cyclohexene yield is not that expected if diffused cyclohexyl radicals were a significant contribution to its formation. Assuming that the conclusions concerning the origin of cyclohexene are valid, it is interesting to note that the relative yields of *t*-butyl cyclohexyl ether


(24)


(25)

---

[38] (a) See P. Wagner and C. Walling, *J. Amer. Chem. Soc.*, **87**, 5179 (1965). (b) The product data (Table III) indicate that β scission of *t*-butoxy has a positive activation volume, as would be expected.

[39] See C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967).

[40] Studies of the product distribution from thermal decomposition of α-cumylazocyclohexane are in progress.

and cyclohexene indicate that coupling and disproportionation of geminate cyclohexyl and *t*-butoxy radicals have essentially the same activation free energies at 80°.

Acknowledgments. Support by the National Science Foundation and helpful discussions with Professors G. S. Hammond, C. Walling, and W. Pryor are gratefully acknowledged. The authors especially thank Professor W. Le Noble for his most generous counsel during the early stages of purchase and assembly of the high-pressure apparatus.

Substitution at a Saturated Carbon Atom. XII. The Generality of the Ion-Pair Mechanism of Nucleophilic Substitution[1]

Richard A. Sneen and John Wester Larsen[2]

Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47907. *Received May 5, 1969*

Abstract: The competitive reactions of solvent water and sodium azide with *p*-methoxybenzyl chloride in 70 vol % aqueous acetone at 20° [3] and of water and *o*-nitroaniline with benzoyl chloride in 50 wt % aqueous acetone at 0° [4] are shown to proceed *via* the ion-pair mechanism of nucleophilic substitution.[5] This article concludes with some general thoughts about the possible consequences and implications of the ion-pair mechanism.

"The Unification of Mechanisms SN1 and SN2" was the perhaps somewhat pompous-sounding title of a recent publication from these laboratories.[5] To be sure although the theory was therein developed which established that a single mechanism, involving as its most distinguishing feature the intermediacy of a configurationally stable ion pair, could accommodate traditional SN1 and SN2 as well as borderline behavior, the operation of this mechanism was demonstrated unequivocally for only two related sets of conditions.

In brief the competitive reactions of solvent water and added azide ion with 2-octyl mesylate in 25 and 30% aqueous dioxane were shown to possess in common an ion-pair intermediate.

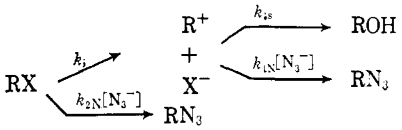
It is of course a rather bold extrapolation, from these limited data, to suggest that all reactions of nucleophilic substitution at a saturated carbon atom proceed *via* an ion-pair mechanism. And yet this is exactly what we would like to suggest. Perhaps data will become available that will require us to modify this view. But we know of none extant to contradict it.

As a further step in establishing the generality of the ion-pair mechanism we herein report reinterpretations of two sets of data taken from the published literature.[3,4]

These additional examples of the ion-pair mechanism not only expand its generality but also serve the rather important ancillary function of providing two new and completely independent methods for the assessment of normal salt effects. This manuscript is concluded with some general thoughts about the possible consequences and implications of the ion-pair mechanism of nucleophilic substitution.

***p*-Methoxybenzyl Chloride.** The competitive reactions of solvent water and azide ion with *p*-methoxybenzyl chloride in 70% aqueous acetone at 20° have been reported by Kohnstam, Queen, and Shillaker.[3] These authors write "sodium azide reduces the rate of hydrolysis (k_h) and increases the rate of ionization (k_i). This . . . demonstrates the unimolecular formation of RN_3. The rate of ionization is, however, always less than the over-all rate of decomposition (k), and it must therefore be concluded that RN_3 is also produced by the alternative, bimolecular mechanism."

Their data are reproduced in Table I. Their presumed reaction scheme can be written



That is, they envisage the operation of distinct competitive uni- and bimolecular reactions.

Table I. Initial First-Order Rate Coefficients (in Sec^{-1}) for the Reaction of 4-Methoxybenzyl Chloride with 70% Aqueous Acetone and Sodium Azide at 20°

[NaN$_3$]		0.0198	0.0312	0.0399
10^4k_h	2.706	2.493	2.427	2.320
10^4k_i[a]	2.706	2.879	2.982	3.063
10^4k	2.706	3.555	4.070	4.336
k_{al}/k_a		0.363	0.338	0.369

[a] By analogy with experiments on diphenylmethyl chloride.

The data, of course, qualitatively fit this picture; quantitatively they do not, even when the scheme is expanded to allow for a second and bimolecular (k_{2s}) pathway for the formation of solvolysis products.[6] In par-

---

(1) Supported in part by the National Science Foundation.

(2) National Institutes of Health predoctoral fellow, 1965–1967.

(3) G. Kohnstam, A. Queen, and B. Shillaker, *Proc. Chem. Soc.*, 157 (1959).

(4) V. Gold, J. Hilton, and E. G. Jefferson, *J. Chem. Soc.*, 2756 (1954).

(5) R. A. Sneen and J. W. Larsen, *J. Am. Chem. Soc.*, **91**, 362 (1969).

(6) They argue against this mode of solvolysis as follows: "hy-